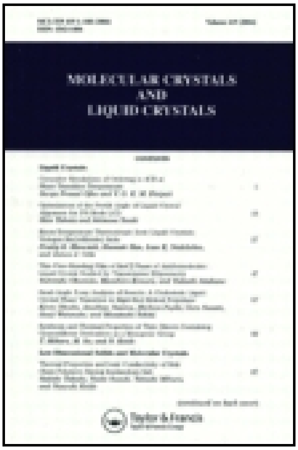

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Induction of Antiferroelectric Phases in High Tilt Chiral Smectics by Doping with Bent-Shaped Liquid Crystals

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Induction of Antiferroelectric Phases in High Tilt Chiral Smectics by Doping with Bent-Shaped Liquid Crystals

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The orthoconic antiferroelectric Sm C_A^* *phase is of high potential for electro-optic applications. Therefore, mixtures of calamitic molecules possessing the Sm* C^* *phase with high tilt angle* ($\Theta \approx 45^\circ$) *and bent core compounds have been prepared. The induction of an antiferroelectric phase has been found even at low concentrations of the banana shaped dopants (5–10 mol%), what has been shown by optic, electro-optic and dielectric investigations. In systems where the host materials possessed the cholesteric and ferroelectric phases, the iso-*N^**-Sm* C^**-Sm* C_A^**-crystal phase sequence has been observed. New materials with perfluorinated end chains exhibiting the Sm A-Sm* C^* *phase transition have shown antiferroelectric phases enveloping the Sm* C^* *phase when doped with biphenyl based bent molecules.*

The tilt angle of the host material remained almost unchanged, i.e. in the case where the host compound possessed a tilt of 45° doping with bent core molecules led to the formation of the orthoconic antiferroelectric liquid crystal.

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Keywords: bent-core molecule; induction of antiferroelectric liquid-crystalline phase; orthoconic antiferroelectric liquid crystal; rod-like molecule; smectic; 45° tilt angle

I. INTRODUCTION

Smectic liquid crystals with antiferroelectric phases, in particular materials with tilt angle of 45° are of high interest because of their potential use in fast electro-optic light modulators. Recently, D́have *et al*. showed, that the antiferroelectric (Sm C_A^*) phase when possessing 45° tilt angle gives rise to the observation of a totally black ground state in surface stabilized planar oriented geometries [1].

Achiral bent core liquid crystals, often called banana shaped, have the advantage of high polarizations (Ps up to 1000 nC/cm^{-2}) and high hyperpolarizabilites leading to strong second harmonic generation [2,3]. Unfortunately it is difficult to align the banana liquid crystals. Only in the case they possess higher temperature phases different from the usual SmCP [4] phases, a more uniform alignment can be achieved.

Recently, Górecka *et al.* [5,6] showed that, in principle, the ferroelectric (Sm C^*) phase of calamitic liquid crystals goes over to the antiferroelectric (Sm C_A^*) phase when doping with small amounts of bent core liquid crystals. The materials used in their study possessed a direct isotropic–Sm C^* phase transition.

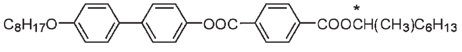
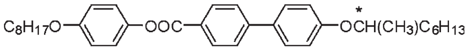
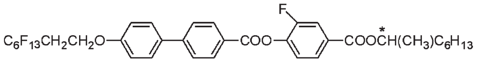
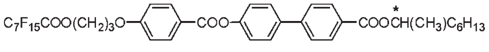
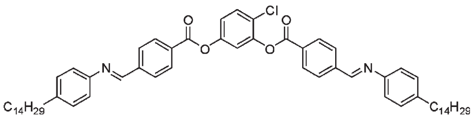
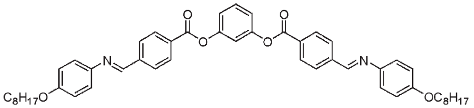
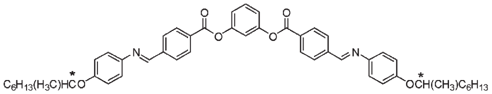
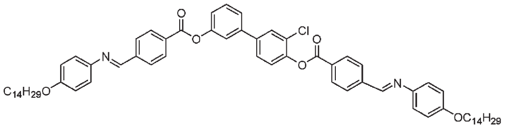
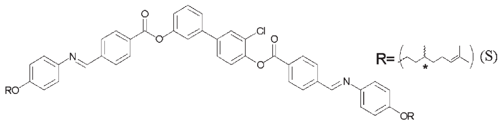
Starting from this point we tried to find out whether it would be possible to induce the antiferroelectric order even in systems with (1) calamitic molecules showing the cholesteric N^*/Sm A^*-Sm C^* phase sequence and (2) possessing high optical tilt angles $\Theta \approx 45°$ what would be of high interest regarding applications. Thus we investigated systems of different calamitic Sm C^* liquid crystals doped with banana shaped compounds. In this contribution the results of dielectric spectroscopy, detailed optical and electro-optical investigations are presented.

II. MATERIALS AND EXPERIMENTAL

The phase transition temperatures of both, pure compounds as well as mixtures, were determined by textural observations using transmitted light polarizing microscope (Leitz SmPolLux) equipped with photodiode and CCD camera and also by differential scanning calorimetry (Perkin–Elmer DSC 7).

All pure calamitic compounds (designated as hosts H1–H4) possess the Sm C^* phase with very high tilt angles ($40° < \theta \leq 45°$). The banana-shaped compounds (designated as dopants D1–D5), except compound D3, show the typical SmCP phases with tilt angles up to 35°. Table 1

TABLE 1 Chemical Structures of Calamitic Host (H1–H4) and Bent-Core Dopant (D1-D5) Materials

name	chemical structure and temperature of phase transitions
H1	 (S) $\text{cryst.} \xrightarrow{80^{O}C} \text{SmC*} \xrightarrow{101^{O}C} \text{N*} \xrightarrow{124^{O}C} \text{iso}$ [7]
H2	 (S) $\text{cryst.} \xrightarrow{81^{O}C} \text{SmC*} \xrightarrow{106^{O}C} \text{N*} \xrightarrow{123^{O}C} \text{iso}$ [7]
H3	 (S) $\text{cryst.} \xrightarrow{85^{O}C} \text{SmC*} \xrightarrow{134^{O}C} \text{SmCá*} \xrightarrow{138^{O}C} \text{SmA} \xrightarrow{162^{O}C} \text{iso}$
H4	 (S) $\text{cryst.} \xrightarrow{62^{O}C} \text{SmC*} \xrightarrow{127^{O}C} \text{SmCá*} \xrightarrow{132^{O}C} \text{SmA} \xrightarrow{155^{O}C} \text{iso}$
D1	 $\text{cryst} \xrightarrow{68^{O}C} \text{SmC}_S\text{P}_A \xrightarrow{127^{O}C} \text{iso}$ [8, 9]
D2	 $\text{cryst.} \xrightarrow{?} \text{B}_4 \xrightarrow{155^{O}C} \text{B}_3 \xrightarrow{162^{O}C} \text{SmC}_S\text{P}_A \xrightarrow{174^{O}C} \text{iso}$ [10]
D3	 $\text{cryst.} \xrightarrow{80^{O}C} \text{iso}$ [11]
D4	 $\text{cryst.} \xrightarrow{105^{O}} \text{SmC}_S\text{P}_A \xrightarrow{174^{O}C} \text{iso}$
D5	 $\text{glass} \xrightarrow{20^{O}C} \text{SmC}_S\text{P}_A/\text{SmC}_A\text{P}_A \xrightarrow{118^{O}C} \text{B}_7 \xrightarrow{122^{O}C} \text{iso}$ [12]

summarizes materialś structures and the polymorphisms of the pure components under investigation.

For dielectric and electro-optic studies the investigated materials were filled to the measuring cells (two glass plates, each covered with conductive (ITO) and planar aligning polymeric layers: one type KSU-cell, Kent State University, US and the other type EHC. Co, Japan) using capillary effects in the isotropic phase. Different cell thicknesses (d = 2, 4, 6, 15 μm) were used. The samples were put in a Linkam hot-stage (type THMS 600) and the temperature was stabilized by Linkam Controller (type TMS 91).

The dielectric spectroscopy as a function of temperature has been carried out in the frequency range f = 100Hz–13MHz using impedance/gain phase analyzer Hewlett–Packard 4194A. The polarization reversal current was investigated as a function of triangular voltage from Keithley Multifunction Synthesizer (3930A) with Krohn–Hite 7500 amplifier and monitored on Gould DSO 1624 oscilloscope. The optical tilt angle was measured using a turn-cell under square applied electric field using the method described in literature [13].

III. RESULTS AND DISCUSSION

In the first investigated system the host material H1 exhibited the ferroelectric Sm C* phase with a tilt angle $\theta = 45^{\circ}$. Mixing with a small amount of dopant (D1–D5) one observed induction of several smectic C* sub-phases. Below we present polarizing micrographs (Fig. 1) taken of one of the investigated mixtures (H1 + 5 mol% D1) filled in a 2 μm

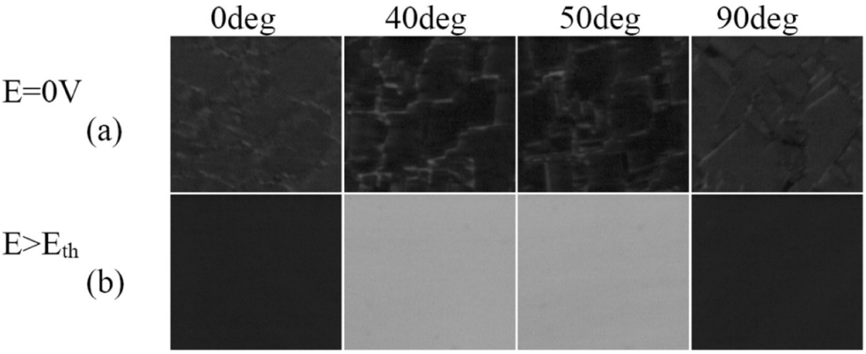


FIGURE 1 Rotation of the H1 + 5 mol% D1 sample in 2 μm planar oriented cell (*KSU-cell*) between crossed polarizers at 63°C without external field (a) and under applied electric field (b).

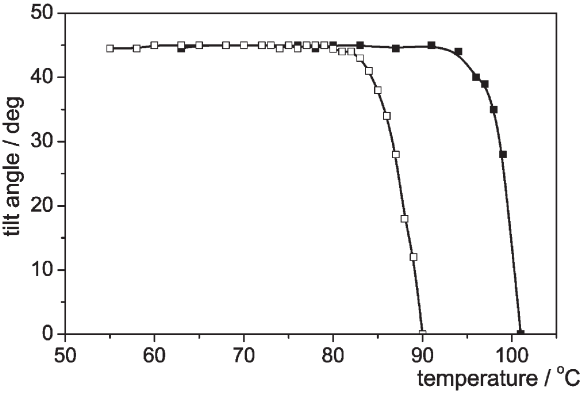


FIGURE 2 Optical tilt angle of the pure H1 material (solid points) and of the H1 + 5 mol% D1 mixture (open points) measured in 2 μm *KSU* cell.

test cell and very slowly cooled under an AC electric field ($E = 1–5\,V/\mu m$) from the isotropic phase.

After removing the electric field at a temperature $T = 63°C$ an almost dark texture with some defect lines was forming. Rotating the test cell in a plane perpendicular to the propagation direction of the polarized light, the intensity of the transmitted light was nearly independent on the angle of rotation (Fig. 1a).

For comparison Figure 1b represents rotation of the same cell but with electric field applied ($E > E_{th}$, where E_{th} denotes the applied electric field necessary for switching from the antiferroelectric to the ferroelectric state). The observed texture did not change until the crystalline phase formed as it was detected during optical tilt measurements (Fig. 2).

The low transmission at zero electric field, which hardly depends on the rotation of the sample, indicates an induction of an alternately tilted SmC_A^*-phase with a tilt angle $\theta \approx 45°$. The assignment additionally is confirmed by the electro-optic response showing tristable switching (Fig. 3a) typical for materials with an antiferroelectric phase [14,15] while in pure H1 material we observed bistable-ferroelectric switching (Fig. 3c), only.

Performing dielectric measurements of the pure compound H1 a Goldstone mode was found. There is no indication of an additional phase transition over the whole temperature range of the Sm C^*-phase. In H1 doped with banana-shaped molecules one did not observe suppression of the Goldstone mode in the ferroelectric phase. The dielectric permittivity below the ferroelectric phase strongly drops down

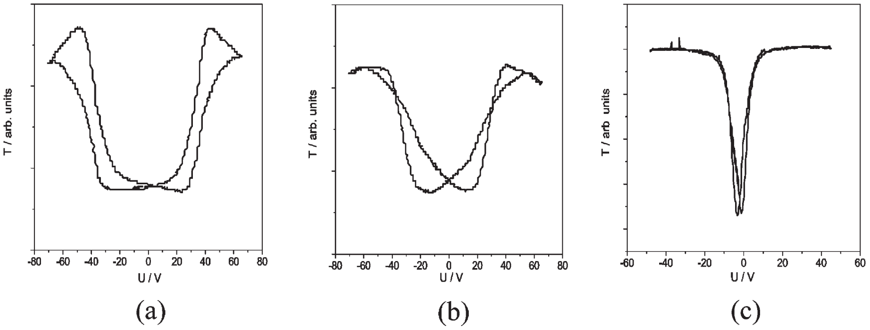


FIGURE 3 Optical transmittance vs. applied electric field measured in 2 μm cell (*KSU-cell*) at frequency 0.02 Hz (a), 0.2 Hz (b) at 60°C for H1 + 5 mol% D1 mixture; and at frequency 0.02 Hz (C) at 63°C for H1 material.

even before crystallization occurs. This is pointing to an induction of Sm Cγ^* and Sm C_A^* phases (see Fig. 4). The transition to the ferroelectric Sm C* phase from the lower temperature phase on heating takes place at higher temperatures than the reverted transition on cooling.

The antiferroelectric dark state (Fig. 1a) and the tristable switching had been observed in this hysteresis range.

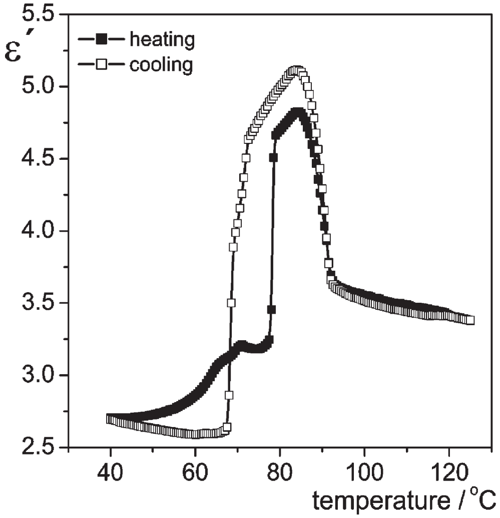


FIGURE 4 Real part of the dielectric permittivity vs. temperature measured at frequency 1 kHz for H1 + 5 mol% D1 mixture (15 μm, *EHC cell*).

The thermal properties of the investigated mixtures also had been studied using a calorimetric method. DSC curves for different molar fractions of H1 + D1 mixtures on heating and one example of cooling process are presented in Figure 5.

As can be seen from Figure 5 there are at least 5 phase transitions indicated by separate peaks in the DSC traces. Using polarization-optical microscopy further phase transitions had been observed and the appropriate phases could be identified from the typical textures. A rich polymorphism has been found. Figure 6 shows a series of micrographs taken for the H1 + D1 mixture.

The investigated mixtures possess broad blue phases (Fig. 6a). In the lower concentration range, until 10 mol% of D1 dopant, TGB phases (Fig. 6b) occurred between N* and Sm C* phases. Additionally, dielectric spectroscopy and textural investigations point to an appearance of a Sm Cα^* phase (Fig. 6c). Textures with moving *Schlierens* at constant temperatures indicates Sm C_γ^* phases (Fig. 6e). The most important phase, the induced Sm C_A^* phase, had been found at low temperatures (Fig. 6f).

A conclusive summary of all optic, calorimetric, dielectric and electro-optic investigations is outlined in a phase diagram (Fig. 7) for concentrations less than 50 mol% of D1.

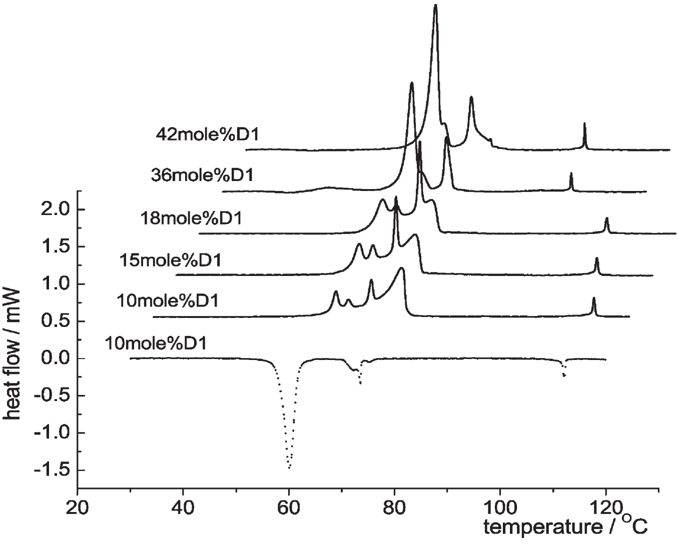


FIGURE 5 DSC thermograms obtained on heating (solid lines) and on cooling (dotted line) for H1 and different mol% of D1 dopant. The scan rates were 3°C/min.

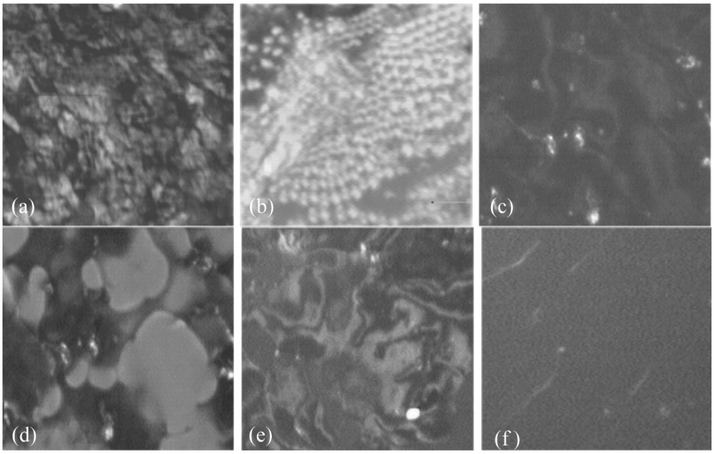


FIGURE 6 Texture series of the H1 + D1 mixtures in homeotropical oriented sample, illustrating the textures changing on cooling from isotropic phase. The following letters coding have been used: a) blue phase; b) TGB phase (in planar oriented sample); c) Sm C* α phase; d) Sm C* phase; e) Sm Cγ* phase; f) Sm C_A^* phase.

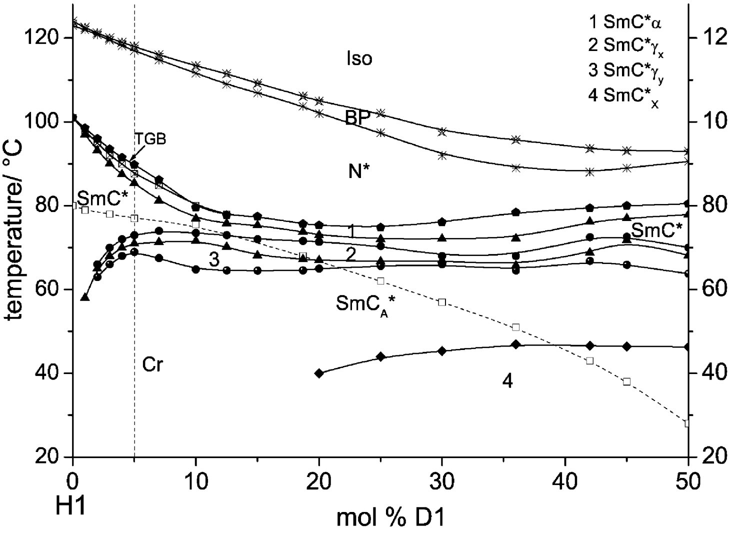
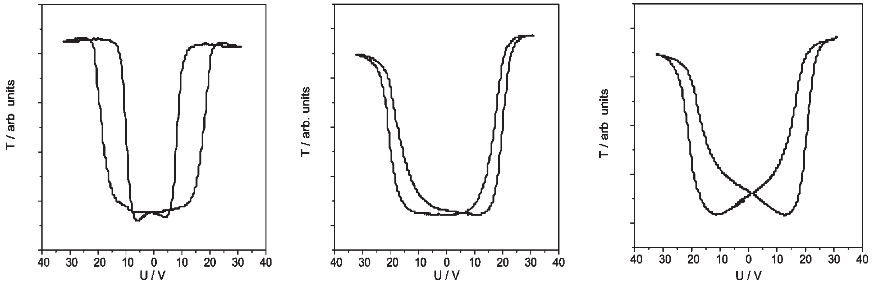


FIGURE 7 The phase diagram for the binary system with the components H1 and D1 investigated until 50 mol% of D1.

It has to be mentioned, that one neither noticed a phase separation on the whole investigated molar fractions nor a direct cholesteric N^*-Sm C_A^* phase transition. Different phases (e.g. Sm C^*) or sub-phases (Sm $C\gamma^*$) always exist between N^*-Sm C_A^*. Moreover, in the system H1 + D1 the antiferroelectric phase is present over a broad concentration range of the banana-shaped dopant (C = 5–50 mol% of D1). As an example the phase sequence on heating of the 10 mol% mixture is as follows (determined from DSC peak temperatures): *cryst.* (76°C) SmC_A^* 64.8°C $SmC^*\gamma y$ 66.9°C $SmC^*\gamma x$ 71.5°C SmC^* 76.9°C $SmC^*\alpha$ 79.5°C *TGB* 80°C N^* 111.6°C *BP* 113.4°C *iso*.

Similar properties have been obtained in the second system, where H2 has been used as the host material. The dielectric spectroscopy of a mixture with 4 mol%D1 also shows thermal hysteresis like the previous one (H1 + 5 mol% D1). In pure H2 material, similar to H1, only bistable switching was observed. In doped mixtures (e.g. 4 mol% D1) tristable switching is present. Figure 8 shows the transmittance of a planar aligned mixture as a function of applied voltage (f = 0.02 Hz) at different temperatures. At 62°C the transmittance of the light passing through the sample is typical for an antiferroelectric material (Fig. 8a). On heating the optical hysteresis transformed and at 75°C the hysteresis nearly vanished. At 80°C the optical traces indicated a phase transition to the ferroelectric phase.

In the case of H1 and/or H2 as host materials and as dopants biphenyl banana-shaped molecules (D4 or D5) [3], no switching up to electric fields higher than 20 V/μm occurred. When rotating the sample between crossed polarizers, the transmittance did not change as it



(a) (b) (c)

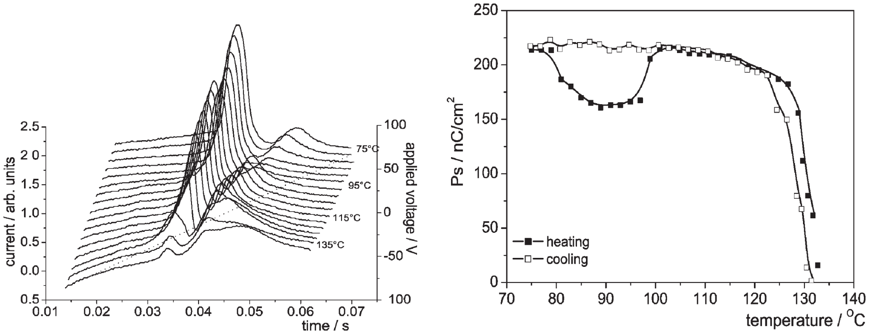
FIGURE 8 Optical transmittance vs applied electric field measured in 2 μm cell (*KSU-cell*) at frequency 0.02 Hz and at a) 72°C, b) 85°C, c) 90°C for H2 + 4 mol% D1.

was observed in the case of the system H1 + 5 mol% D1. Additionally, the dielectric spectra were similar. Thus we conclude that even in this case the Sm C_A^* phase was formed but the threshold was too high for switching.

In contrary using H3 or H4 as hosts doped with a small amount of biphenyl-based dopant (D4 or D5) switching of the sample was possible. The current response obtained under application of a triangular electric field with a frequency of 2 Hz for a mixture of H3 + 10 mol% D4 D4 is shown in Figure 9a.

One can see that in the whole temperature range the current response exhibits two well separated peaks. The total area of the two apparent peaks in cooling shows the typical temperature behavior of tilted smectic phases of chiral calamitic molecules, e.g. the behavior of the Sm Cx* phases. The calculated spontaneous polarization ($P_{Smax} = 240\,nCcm^{-2}$) is about twice as high as that of the pure H3 material. In contrary, when heating the sample, the current response shows a drop down of the spontaneous polarization in a temperature range ΔT = 85–100°C (Fig. 9b). In this range the material exhibited an optical characteristic of an almost bistable switching. Below a temperature of 85°C Ps showed again increased values. A similar behavior has already been reported for pure biphenyl based banana shaped molecules [16].

The dielectric spectra reflect the behavior of the current responses. As can be seen from Figure 10 in the already mentioned temperature range (ΔT = 85–100°C) there is a strong increase of the imaginary part of the dielectric constant. At higher temperatures (T > 100°C) a mode



(a) (b)

FIGURE 9 Current response (a) and spontaneous polarization (b) obtained for H3 + 5 mol% D4 mixture.

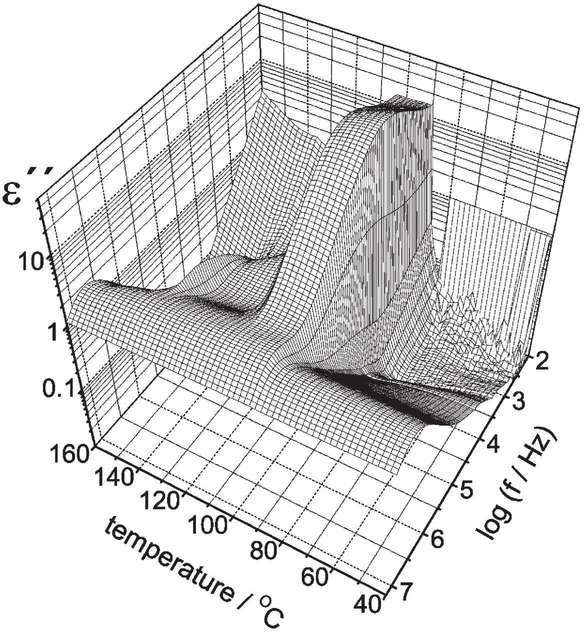


FIGURE 10 The imaginary part of the dielectric permittivity for H3 + 5 mol% D4 mixture measured on heating (15 μm *EHC cell*).

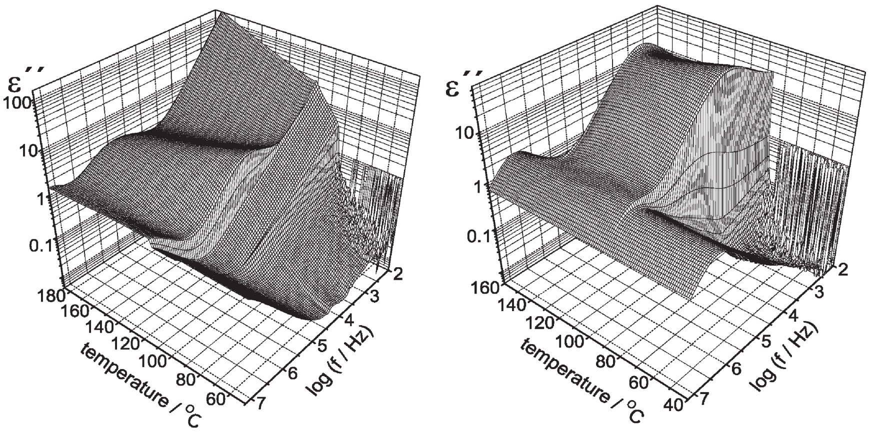
($\Delta\varepsilon = 0.4$ at $T = 114$°C) was observed showing a strong temperature dependence of the corresponding relaxation frequencies.

Assuming a simple Arrhenius behavior an activation energy of about 80 kJ/mol was calculated.

For comparison the spectra of the pure materials are depicted, too (Fig. 11a). The dopant D4 shows the typical behavior of the SmC_SP_A phase [17,18], whereas the host possessed the spectrum of a typical Sm C* phase with Goldstone mode (Fig. 11b).

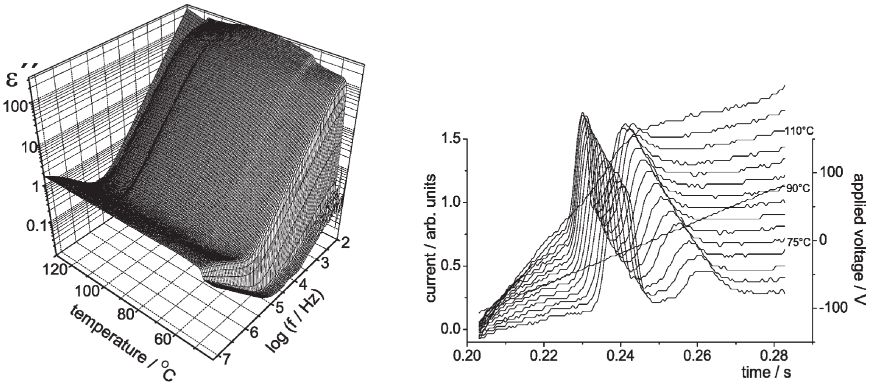
Strikingly the temperature behavior of the observed relaxation mode of the dopant D4 is similar to that of the mixture in the temperature range higher than 100°C. But the absolute relaxation frequencies are shifted to higher values when compared to the doped material.

The system H3 + D5 showed similar properties. All other systems (host H3 + D1, D2 and D3 and H4 + D1–D5) exhibited high dielectric constants in the range of the tilted smectic phases (Fig. 12a). But here a double peak in the current response to a triangular electric field was found indicating antiferroelectric like behavior (see Fig. 12b).



(a) (b)

FIGURE 11 The imaginary part of the dielectric permittivity for D4 (a) and H3 (b) compounds measured on heating (15 μm *EHC cell*).



(a) (b)

FIGURE 12 The imaginary part of the dielectric permittivity (a) and current response (a) for H4 + 5 mol% D1 mixture measured on cooling.

IV. SUMMARY

Different rod like materials doped with bent core molecules have been investigated. In all combinations depending on the concentration of the bent core dopant one found antiferroelectric-like switching behavior. In particular, in the systems H1 or H2 + D1 one observed that the antiferroelectric phase SmC_A^* formed at concentrations of about 5–50 mol% of the bent core dopant. Moreover the optical tilt angle appears to be independent of the amount of the dopant what means that the tilt angle of the host SmC^* materials remains unchanged also in the antiferroelectric phase. In particular, in a material with tilt angle of 45° the antiferroelectric ground state possessed nearly no change of transitivity with rotation of the sample with respect to the crossed polarizes. Additionally, the observed thermal hysteresis of Sm C^*-Sm C_A^* phase transition during heating and cooling cycles is typical for mixtures with induced antiferroelectric phases [19]. A direct N^*-Sm C_A^* phase transition had not been observed. Different phases (e.g. Sm C^*) or sub-phases (Sm $C\gamma^*$) always exist between N^*-SmC_A^*. In same cases with host H1 and biphenyl bent molecules as dopants the threshold was too high for switching.

In systems where the host materials possessed perfluorenated end chains (H3 or H4) a totally different electro-optic and dielectric behavior has been found when compared to the pure host materials. In particular textures as well as the dielectric properties resemble those of the banana shaped dopants. One could speculate that in these cases the system has the tendency to form bilayers thus even in low concentration of the banana shaped dopant could be sufficient to induce typical banana phases. In contrary, the pure hosts possessed the Sm C^* phase with Goldstone mode only.

Further investigations, i.e. detailed X-ray investigations have to be carried out to give substantial evidence for this hypothesis.

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